

Public

# FUEL AND FUEL ADDITIVE REGISTRATION TESTING FOR NESTE OIL CORPORATION

## FINAL REPORT

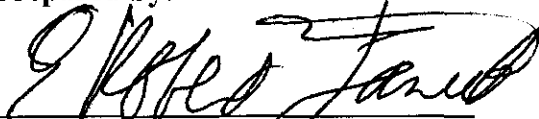
SwRI® Project No. 03.13200rev.

Prepared for:

Neste Oil Corporation  
1800 West Loop South  
Suite 1700  
Houston, TX 77027

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Prepared by:

  
E. Robert Fanick, Group Leader

Approved by:

  
Jeff N. White, Director

EMISSIONS RESEARCH AND DEVELOPMENT DEPARTMENT  
ENGINE, EMISSIONS, AND VEHICLE RESEARCH DIVISION

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Results and discussion given in this report relate only to the test items described in this report.

## **IDENTIFICATION OF TEST SUBSTANCE**

Neste Oil Corporation is a refining and marketing company focused on advanced, clean traffic fuels, with a strategy that prioritizes growing its refining and premium-quality renewable diesel businesses. Neste Oil Corporation's refineries are located at Porvoo and Naantali in Finland, and have a total refining capacity of approximately 250,000 bbl/day. The company employs around 4,800 people, and its shares are listed on the Nordic Exchange Helsinki.

NExBTL™, produced by Neste Oil Corporation, is the cleanest renewable diesel fuel available today. It offers significant reductions in both lifecycle greenhouse gas emissions and tailpipe emissions compared to petroleum diesel fuel. The precise reductions in greenhouse gases depend on the raw materials used in production. Tests have shown NExBTL™ to produce 40-60% less CO<sub>2</sub> throughout the whole product lifecycle. NExBTL™ can be used neat (100%) or blended to any concentration, and it does not require modifications to the existing vehicle pool.

## **MANUFACTURER**

**Neste Oil Corporation  
1800 West Loop South  
Suite 1700  
Houston, TX 77027**

## **CONTACT PERSON**

**Mr. Neville Fernandes  
Phone: (713) 584-5244**

## FOREWORD

This project was performed for Neste Oil Corporation under SwRI Project 03-13200. Mr. Neville Fernandes was the technical representative for Neste Oil Corporation. The Principal Investigator and the Project Leader was Mr. E. Robert Fanick, Group Leader in the Emissions Research and Development Department. SwRI technical personnel involved in heavy-duty engine operation and emissions testing included: Mr. Tim Milligan, Richard Mendez, Ms. Kelley L. Strate, and Ms. Yolanda Rodriguez. Data reduction was performed by Ms. Kathleen M. Jack, Ms. Sylvia G. Nino, Ms. Amanda L. Korzekwa, and Ms. Linda De Salme. The SwRI Project Manager for this work was Dr. Lawrence R. Smith, Manager of the Chemistry and Unregulated Emissions Section. Southwest Research Institute is located at:

6220 Culebra Road  
P.O. Drawer 28510  
San Antonio, TX 78228-0510  
Phone: (210) 684-5111

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## TEST SUBSTANCE INFORMATION

The NExBTL™ renewable diesel process was developed by Neste Oil Corporation of Finland to make renewable diesel. This process has been designed to take advantage of the infrastructure of a refinery and to produce pure hydrocarbons of the high quality. In the NExBTL™ renewable diesel process, animal fats and vegetable oils (triglycerides) are converted into diesel fuel components. The process utilizes all types of vegetable oils as well as all kinds of animal greases and fats. All of these oils and fats have a similar chemical structure which is comprised of three fatty acid chains joined to a glycerol to form a triglyceride. Neste Oil Corporation has conducted many bench scale tests and pilot runs, and it has been shown that all feedstock will produce high quality diesel fuel. NExBTL™ renewable diesel can be used neat (100%) or blended to any concentration, and it does not require modifications to the existing vehicle pool.

The process steps utilized in the NExBTL™ technology were adapted from normal refinery processes. The process steps are:

- Feedstock Pre-treatment, in which contaminants are reduced to very low levels
- Hydrotreating where oxygen is removed, and paraffins are formed and branched
- Product finishing and stabilization

In the pre-treatment step, commercial vegetable oil de-gumming technology is used. This de-gumming technology was adapted to achieve the purity levels required to maintain a long catalyst lifetime. In the hydrotreating stage, hydrogen is fed into the reactor vessel under pressure together with the feedstock. The resulting product is an iso-paraffin with significantly improved cold flow properties, lowering the cloud point from to -25°C or even lower. The severity of this process step is controlled depending on the grade of fuel required. More severe process conditions are used to produce a winter diesel with superior cold properties.

The chemical composition of the resultant renewable diesel is a combination of straight and branched chain paraffins or alkanes. The straight and branch chain paraffin speciation in NExBTL™ is determined by a variety of analytical techniques including gas chromatography and mass spectrometric analyses. The carbon numbers in NExBTL™ renewable diesel range from C<sub>10</sub>-C<sub>20</sub>, and the boiling range is from 120°C to 320°C which is the same as diesel produced from crude oil. The final product contains no oxygen (<0.01%), no sulfur (<0.001%), no nitrogen, and has a very low content of aromatics (<<0.02%). The hydrocarbons that are produced in the NExBTL™ renewable diesel process are the same as those already present in diesel produced from crude oil. There are no aromatic hydrocarbons, and only the relative concentration of the straight chain (n-paraffin) and branched chain paraffins (iso-paraffin) is increased.

Extensive engine and vehicle testing have been performed using NExBTL™ renewable diesel in a variety of diesel engines and cars. Both regulated and non-regulated emissions have been measured. Exhaust emissions of the oxides of nitrogen (NO<sub>x</sub>), particulate matter (PM), hydrocarbons (HC) and carbon monoxide (CO) are all reduced significantly compared with emissions from “traditional” diesel produced from crude oil. Heavy duty engine emissions using

“neat” NExBTL™ renewable diesel were compared with engines using European sulfur-free EN590-diesel grade. The exhaust emissions when using NExBTL™ renewable diesel showed remarkable reductions:

- NO<sub>x</sub> reduction of 7% to 14%;
- Particulate reduction of 28% to 46%;
- CO reduction of 5% to 78%;
- Hydrocarbon reduction of 0% to 48%;
- Source: SAE Paper No. 2007-01-4031

Similarly, NExBTL™ renewable diesel blended in EN-590 diesel fuel has shown emission reductions in tests done using diesel passenger cars. A blend of 85 % NExBTL™ in EN-590 diesel showed the following emission reductions:

- Particulate reduction of 17% to 30%;
- CO and HC reduction of 45% to 55%;
- Formaldehyde and acetaldehyde reduction of 40% to 45%;
- Benzene and 1,3-butadiene reduction of 40% to 45%;

Particulate composition analyses showed a reduction in polyaromatic hydrocarbons (PAHs), as well as lower mutagenicity (SAE Paper No. 2005-01-3771).

In addition, NExBTL™ renewable diesel offers significant reductions in lifecycle greenhouse gas emissions compared to petroleum diesel fuel. The precise reductions in greenhouse gases depend on the raw materials used in production. Tests have shown NExBTL™ to produce 40 to 60% less greenhouse gas emissions throughout the whole product lifecycle.

NExBTL™ renewable diesel properties can be summarized as follows:

- The carbon chain length in NExBTL™ is within the range (C<sub>10</sub>-C<sub>20</sub>) of “traditional” diesel produced from crude oil;
- The boiling range (120°C to 320°C) of NExBTL™ is within the range of “traditional” diesel;
- Extensive engine and vehicle testing has been performed in a variety of diesel engines, and NExBTL™ has shown superior fuel properties compared with “traditional” diesel;
- Due to the absence of sulfur and aromatic compounds, NExBTL™ exhaust emissions show significant reduction of many regulated and non-regulated compounds compared with “traditional” diesel.

## EXECUTIVE SUMMARY

The NExBTL™ renewable diesel was evaluated for Neste Oil Corporation in support of the Environmental Protection Agency (EPA) requirements for registration of designated fuels and fuel additives (F/FA) as stipulated by sections 211(b) and 211(e) of the Clean Air Act (CAA). Under the Tier I requirements of this protocol, manufacturers of F/FAs are required to supply EPA with:

- The identity and concentration of emission products from the F/FA
- An analysis of potential emissions exposures
- Any available information regarding the health and welfare effects of the whole and speciated emissions.

As a result, emission generation, collection, and analysis of the regulated emissions and of selected vapor- and particulate-phase unregulated emissions, and a speciation of volatile-phase hydrocarbon compounds were performed on a 2007 6.4 L Navistar A350 engine. The engine was first tested after 125 hours of engine operation with only the baseline fuel. Testing involved a cold- and six hot-start test sequence on each of three different days with the aftertreatment installed and once again with the aftertreatment removed. Samples were collected and analyzed for regulated emissions including total hydrocarbons (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), and total particulate; for a hydrocarbon speciation; for selected vapor- and particulate-phase compounds; and for volatile- and particulate-phase polycyclic aromatic hydrocarbons (PAH) and nitrated polycyclic aromatic hydrocarbons (NPAH). The fuel was then changed to neat NExBTL™ renewable diesel. The engine was operated for 125 hours with neat NExBTL™. At the completion of the durability engine operation, the above emission characterization test sequence was repeated.

In general, the engine was able to meet the 2007 emissions standard for the baseline tests with aftertreatment. The 2007 emissions standards limit the sum of NO<sub>x</sub> and NMHC (NO<sub>x</sub> + NMHC) to 2.4 g/bhp-hr or to 2.5 g/bhp-hr if the NMHC do not exceed 0.5 g/bhp-hr. The limit for particulate emissions is 0.10 g/bhp-hr. In this case, the baseline composite emissions were 1.0 g/bhp-hr for NO<sub>x</sub> and 0.02 g/bhp-hr for NMHC with the aftertreatment and 1.0 g/bhp-hr for NO<sub>x</sub> and 0.18 g/bhp-hr for the NMHC with the aftertreatment removed. The NO<sub>x</sub> + NMHC with aftertreatment was 1.0 g/bhp-hr and 1.2 g/bhp-hr without aftertreatment. Composite particulate emissions for the baseline tests were 0.01 g/bhp-hr with aftertreatment and 0.31 g/bhp-hr with the aftertreatment removed. After 125 hours of engine operation with neat NExBTL™ renewable diesel, the NO<sub>x</sub> emissions were about 17 percent lower with aftertreatment and 13 percent lower without aftertreatment when compared to the baseline fuel. The NO<sub>x</sub> + NMHC was 0.8 g/bhp-hr with aftertreatment and 1.0 g/bhp-hr without aftertreatment. No change was noted for the particulate with aftertreatment, and a 6 percent reduction was observed without aftertreatment.

When the speciated emissions from the baseline fuel were compared to neat NExBTL™ renewable fuel, no additional C<sub>1</sub> to C<sub>12</sub> hydrocarbons, aldehydes, and ketones were present in the exhaust above the detection limits of the analytical procedures. In general, all compounds found



in the exhaust with neat NExBTL™ renewable diesel were also found in the exhaust with the baseline fuel. A number of compounds were detected in the tests with the baseline diesel fuel that were not detected in the tests with neat NExBTL™ fuel. Some compounds were found in tests with the aftertreatment removed, but not with the aftertreatment in place. This observation was noted for tests with both fuels. In any case, no additional compounds, which could be attributed to the presence of NExBTL™ fuel, were found in the exhaust at the detection limits for the analytical procedures.

Volatile- and particulate-phase PAH and NPAH were not required in this study, but samples were collected at the request of Neste Oil Corporation. Analyses were conducted for individual compounds including: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene. In general, the particulate-phase PAH and NPAH concentrations were higher than the volatile-phase compounds. Higher concentrations of PAH and NPAH compounds were detected for both fuels when the aftertreatment was removed. The total PAH and NPAH were higher with the baseline fuel and lower with the neat NExBTL™ renewable diesel.

## 1.0 INTRODUCTION

This work was performed for Neste Oil Corporation in support of the Environmental Protection Agency (EPA) requirements for registration of designated fuels and fuel additives (F/FA) as stipulated by sections 211(b) and 211(e) of the Clean Air Act (CAA). In general, standard mandatory requirements for F/FA registrations are contained in a three tiered structure. The first two tiers generally apply to most F/FA manufacturers, but there are special provisions for certain types of additives and small businesses. Each manufacturer is required to submit basic registration data for each product being registered. Small businesses with less than \$50 million of annual sales are excused from the first two tiers of requirements for F/FA which are considered baseline or non-baseline, and small businesses with less than \$10 million annual sales are excused from Tier 2 requirements for "atypical" F/FA. Definitions of baseline, non-baseline, and "atypical" F/FA are discussed in detail below. Other special provisions include experimental F/FA, relabeled products, and products exclusively for off-road use.

Each F/FA is sorted into one of two broad "fuel families": conventional or alternative. The conventional fuel families are gasoline and diesel, and the alternative fuel families include methanol, ethanol, methane, and propane. Each fuel family is then subdivided into three "F/FA categories": baseline, non-baseline, and "atypical." The baseline category consists of fuels and associated fuel additives which resemble the respective baseline fuel for a particular fuel family in terms of elemental composition (no elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur), and which conforms with certain quantitative limits for particular constituents. "Atypical" is defined as those which contain metals; elements other than carbon, hydrogen, nitrogen, sulfur, and oxygen; or do not meet the requirements under ASTM D975 "Standard Specifications for Diesel Fuel Oils." The non-baseline category is an intermediate category between baseline and atypical. In the diesel fuel family, the distinction between baseline and non-baseline is based primarily on the presence of significant concentrations of oxygen-containing compounds (greater than 1.0% oxygen by weight).

Tier 1 testing for the generation, collection, and analysis of combustion emission samples was required. Regulated exhaust emissions for total hydrocarbons (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), and particulate (PM) and carbon dioxide (CO<sub>2</sub>) were evaluated for all tests conducted. In addition, a hydrocarbon speciation was performed to determine volatile-phase exhaust hydrocarbons, aldehydes, and ketones; and samples were collected for volatile- and particulate-phase polycyclic aromatic hydrocarbons (PAH) and nitrated polycyclic aromatic hydrocarbons (NPAH). This report includes the emission measurements that were conducted as part of the requirements for the registration of an additive or fuel as stipulated by sections 211(b) and 211(e) of the CAA.

## 2.0 HEAVY-DUTY ENGINE TESTING

### 2.1 Objective

The objective of this program was to provide Neste Oil Corporation with the generation, collection, and analysis of combustion emission samples from a renewable diesel called NExBTL™ using a 2007 6.4 L Navistar A350 engine. For comparison purposes, emission testing was performed with a baseline fuel that met the specifications in Title 40 Code of Federal Regulations (CFR) Part 79, Subpart F, Section 79.55 and with the neat NExBTL™ renewable diesel. Emission testing was conducted according to Tier 1 requirements as identified in Title 40 CFR Part 79, Subpart F, Section 79.57. Protocols outlined in Title 40 CFR Part 86, Subpart N and in applicable Southwest Research Institute® (SwRI)® Test and Inspection Procedures (TIP) References 1 through 17 were followed.

### 2.2 Scope of Work

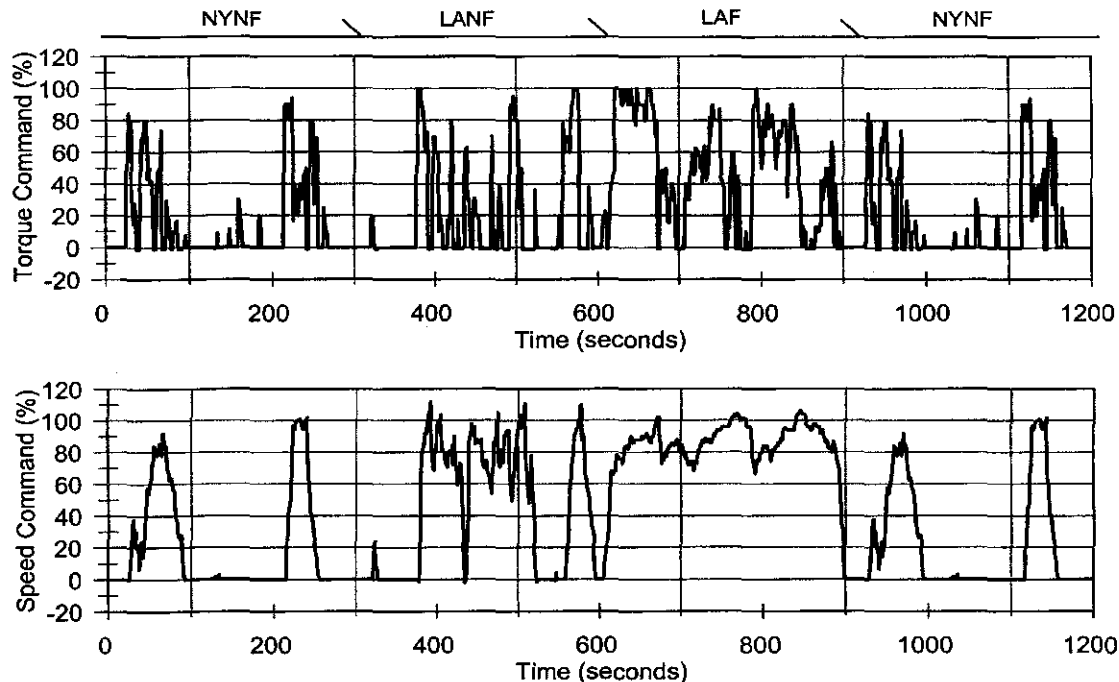
#### 2.2.1 Heavy-Duty Test Protocol

Tier 1 testing for fuel and fuel additive registration requires the EPA transient test protocol. Prior to testing, the engine was operated for 125 hours to “break-in” the engine. Emission testing was then performed on the engine at the 125-hour point with the baseline fuel. Testing consisted of cold- and hot-start EPA transient sequences with one cold- and six hot-start tests performed on each day. Three test sequences were performed with the diesel particulate filter (DPF) in place and three with the aftertreatment removed (a spool piece was installed in place of the DPF). At the completion of the baseline testing, the fuel was changed to neat NExBTL™ renewable diesel fuel. Durability engine operation was performed for an additional 125 hours of engine operation, and the emissions characterization test sequence with was repeated. Table 1 presents the test plan for the fuel evaluations conducted in this study.

The EPA transient cycle or Federal Test Procedure (FTP) is described by means of percent of maximum torque and percent of rated speed for each one-second interval over a test cycle of 1199 seconds duration. To generate a transient cycle, an engine's full load torque curve is obtained from an engine speed below curb idle speed to maximum no-load engine speed. Data from this "torque curve," or torque map, are used with the specified speed and load percentages to form a transient cycle. A graphic presentation of the speed and torque commands which constitute a transient cycle is given in Figure 1 for illustration purposes. The first five minutes of the cycle is designated as the New York Non-Freeway (NYNF) portion of the test and represents city operation with extensive idle time. The second five minutes is called the Los Angeles Non-Freeway (LANF) portion. This part of the test also represents city operation, but without the excessive idle time. The third five minute section of the test is called the Los Angeles Freeway (LAF) portion. This part is more representative of higher speed conditions indicative of freeway operation. The final five minutes of the EPA transient cycle is a repeat of the NYNF portion. These four parts are combined to give the EPA transient cycle.

**TABLE 1. TEST PLAN FOR HEAVY-DUTY TESTING**

Step	Description
1	Perform emission instrument calibrations as required. Calibrate torque meter and check signal conditioning systems. Validate Constant Volume Sampler (CVS) gaseous and particulate sampling systems using propane recovery techniques.
2	Install engine in transient-capable test cell and check engine condition. Engine must be <u>new</u> with less than 12 hours of previous operation. Bring engine oil level to "full" using oil specified by the manufacturer.
3	Perform fuel change procedure to baseline diesel fuel. Change fuel filters, purge fuel supply, etc. ( <b>Note:</b> No other fuel should be used until testing with this fuel has been completed.) Perform 125 hours of engine operation with the baseline diesel fuel. If unscheduled maintenance is necessary, the repairs will be made to Original Equipment Manufacturer (OEM) specifications using OEM or OEM approved parts. In addition, emissions should be measured after any unscheduled maintenance and before resuming durability, to ensure that post-maintenance emission levels are within $\pm 20$ percent of the pre-maintenance emission levels.
4	Repeat Step 1 as necessary. Operate engine at rated speed and full load for approximately 10 minutes, then power validate engine.
5	Conduct transient "full-throttle" torque map from low- to high-idle and save resulting transient command cycle.
6	Run a 20-minute practice EPA transient cycle without engine-off soak between cycles, and adjust dynamometer controls to meet statistical requirements for transient cycle operation.
7	Soak engine overnight. Run a cold-start transient cycle. Soak engine for 20 minutes. Run six hot-start transient cycles with a 20 minute soak between each cycle. Collect samples for THC, CO, NO <sub>x</sub> , total particulate, speciation of volatile hydrocarbon compounds, aldehydes, ketones, PAH, and NPAH during each cycle.
8	Repeat Step 7 two additional times on different days.
9	Repeat steps 4 through 8 with the aftertreatment device removed and a blank spool piece in place of the aftertreatment device.
10	Perform fuel change procedure to neat NExBTL™ renewable diesel. Change fuel filters, purge fuel supply, etc. ( <b>Note:</b> No other fuel should be used until testing with this fuel has been completed.) Perform engine operation for 125 hours. If unscheduled maintenance is necessary, the repairs will be made to Original Equipment Manufacturer (OEM) specifications using OEM or OEM approved parts. In addition, emissions should be measured after any unscheduled maintenance before resuming durability, to ensure that post-maintenance emission levels are within $\pm 20$ percent of the pre-maintenance emission levels
11	Repeat Steps 4 through 9.



**FIGURE 1. GRAPHIC REPRESENTATION OF TORQUE AND SPEED COMMANDS FOR THE EPA TRANSIENT CYCLE FOR HEAVY-DUTY ENGINES**

In general, a transient test consists of both cold- and hot-start EPA transient cycle operation. The same engine command cycle is used in both cases. For the cold-start, the diesel engine is operated over a "prep" cycle and then allowed to stand overnight in an ambient soak at a temperature between 68 and 86°F. The cold-start transient cycle begins when the engine is cranked for cold start-up. Upon completion of the cold-start transient cycle, the engine is stopped and allowed to stand for 20 minutes. After this hot-soak period, a hot-start EPA transient cycle begins with engine cranking. In order to determine how well the engine followed the transient command cycle, engine performance is compared to engine command, and several statistics are computed. These computed statistics must be within tolerances specified in the CFR. In addition to statistical parameters, the cycle work actually produced should be between 5 percent above and 15 percent below the work requested by the command cycle.

### **2.2.2 Heavy-Duty Engine Selection and Description**

For the purpose of testing the NExBTL™ renewable fuel, a 2007 6.4 L Navistar A350 engine (Serial No. 7046094) was selected and purchased for Neste Oil Corporation. Engine model and family were accepted by Mr. Jim Caldwell in an e-mail to Mr. Neville Fernandes on May 8, 2007. The engine was selected to meet the following criteria:

- Less than 12 hours on the engine chronometer
- Same type, class, and subclass which consumed the most gallons of fuel in the fuel family over the past three years

- Represent the most common fuel metering system and the most common of the most important emission control system devices or characteristics with respect to the emission reduction performance for the model year in which testing began
- One of the five highest selling models from the current model year
- Unaltered from the specification of the original equipment manufacturer and to remain under the control of SwRI throughout the testing.

Table 2 lists the engine specifications and features.

**TABLE 2. ENGINE SPECIFICATIONS AND FEATURES**

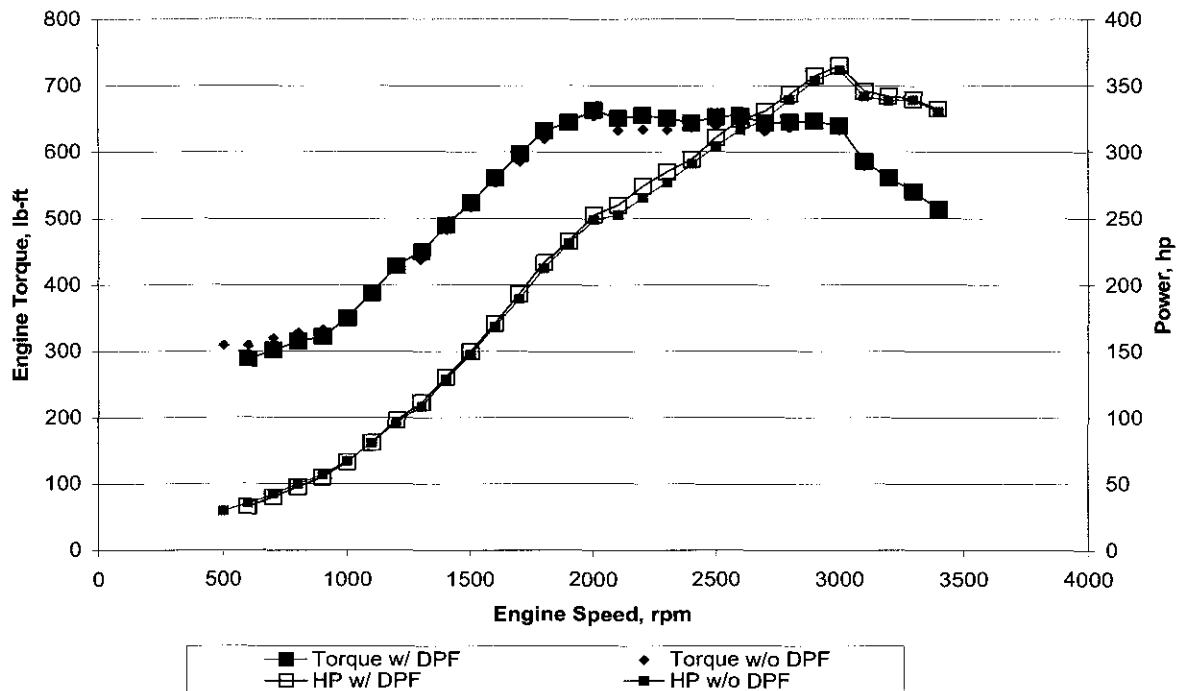
<b>Engine Parameter</b>	<b>Comment</b>
Engine Type	Diesel, 4-Cycle
Model	A350
Serial No.	7046094
Configuration	V-8
Displacement	6.4L 366 (CID)
Aspiration	Turbocharged
Rated Power at rpm	350hp at 3000 rpm
Peak Torque at rpm	650 lb-ft at 2000 rpm
Idle Speed	700 rpm
Combustion System	Direct Injection, Turbocharged, Electronic Control Module, Charge Air Cooling, Exhaust Gas Recirculation
Engine Family	7VXH06.4AGC
Aftertreatment	Oxidation Catalyst/Diesel Particulate Filter

### **2.2.3 Durability Cycle and Engine Mapping**

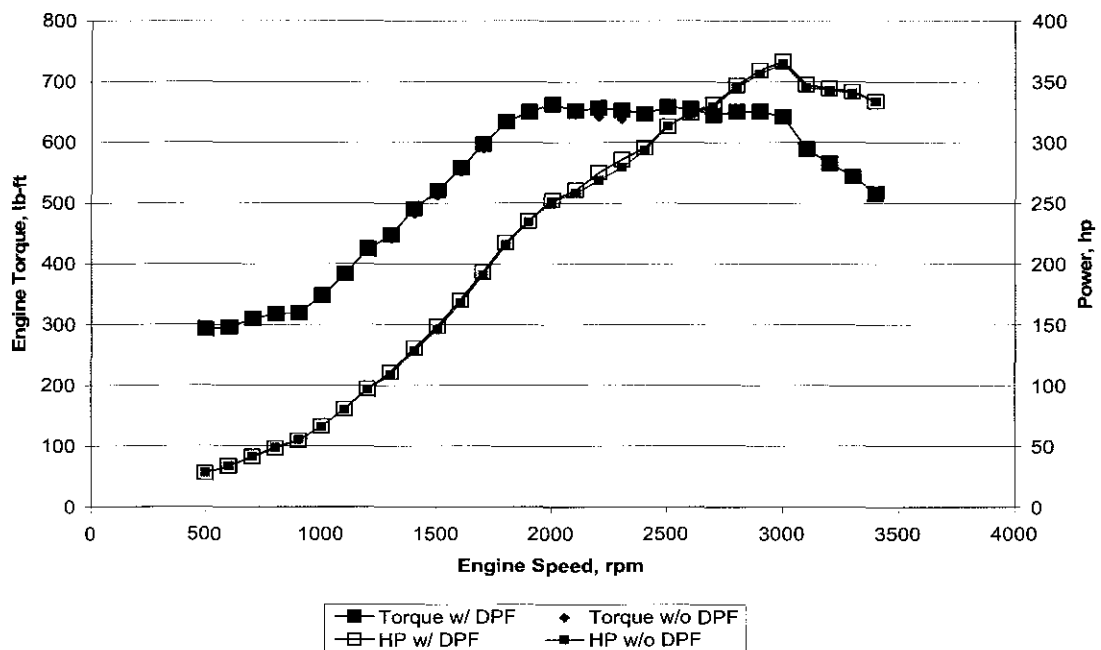
After the engine was received, it was operated for 125 hours with the baseline fuel using a proprietary durability cycle obtained from Navistar. This durability cycle was conducted on a continuous basis to obtain the designated hours of engine operation without aftertreatment. This request was made for technical reasons which were identified in an e-mail to Mr. Jim Caldwell. Approval to perform the durability without aftertreatment was provided by Mr. Jim Caldwell on May 22, 2007. The same proprietary durability cycle without aftertreatment was used with each fuel. Emission testing was performed after 125-hour of engine operation with each fuel. Figures 2 and 3 illustrate the engine map used for the baseline and for the neat NExBTL™ renewable diesel.

### **2.2.4 Fuel Blending and Analyses**

The baseline fuel used for durability and testing was obtained in two batches from Halterman Products. These two batches were designated as EM-6492-F and EM-6541-F. EM-6541-F was used for the emission testing only, while EM-6492-F was used for the durability. Both fuels had less than 15 ppm sulfur for 2007 model engines due to the use of an



**FIGURE 2. SPEED AND TORQUE MAP FOR BASELINE FUEL AFTER 125 HOURS OF DURABILITY**



**FIGURE 3. SPEED AND TORQUE MAP FOR THE NEAT NexBTL™ RENEWABLE DIESEL AFTER 125 HOURS OF DURABILITY**

aftertreatment system which could not tolerate higher sulfur concentrations. A waiver was obtained from Mr. Jim Caldwell on May 2, 2007 to use an ultra-low sulfur fuel in place of the previously required low sulfur fuel. All other fuel properties were able to meet the 211(b) specifications. The neat NExBTL™ renewable diesel was designated EM-6514-F. Table 3 presents the test fuel properties and the 211(b) test fuel specifications for comparison.

**TABLE 3. FUEL ANALYSIS**

Fuel Property	211(b) Specifications for Baseline Fuel	Analytical Results		
		EM-6492-F <sup>a</sup>	EM-6541-F <sup>b</sup>	EM-6514-F
API Gravity	33±1	34.0	33.3	49.8
Sulfur, ppm	<15	10	6	0.2
Cetane Number	45.2±2	42.0	42.8	>75 <sup>c</sup>
Cetane Index	45.7±2	42.2	42.8	77.1
Aromatics, vol %	38.4±2.7	36.3	37.0	ND <sup>d</sup>
Olefins, vol %	1.5±0.4	1.6	1.6	ND
Saturates, vol %	60.1±2.0	61.1	61.4	ND
<b>Distillation</b>				
10%, °F	433±5	404	414	525
50%, °F	516±5	487	499	543
90%, °F	606±5	598	602	566
<b>Required Additives</b>				
Corrosion Inhibitor, ptb <sup>e</sup>	Required	4.5	4.5	NA <sup>f</sup>
Demulsifier, ptb	Required	2	2	NA
Anti-oxidant, ptb	Required	2	2	NA
Metal Deactivator, ptb	Required	2	2	NA
<sup>a</sup> Baseline durability fuel <sup>b</sup> Baseline emissions fuel <sup>c</sup> Reported as greater than 75 because actual value was greater than the secondary reference fuel <sup>d</sup> ND – Not determined <sup>e</sup> ptb-pounds per thousand barrels <sup>f</sup> NA – No additives				



### 3.0 DESCRIPTION OF ANALYTICAL METHODS

Regulated and unregulated emission measurements conducted for this program, as required by the EPA, included the following:

- Measurement of regulated emissions including THC, CO, NO<sub>x</sub>, and total particulate,
- Speciation of volatile-phase hydrocarbon compounds, aldehydes, and ketones,
- Semi-volatile emissions for both volatile- and particulate-phase PAH and NPAH including: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene, 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene,

Regulated emissions (THC, CO, NO<sub>x</sub>, and particulate) and CO<sub>2</sub> were analyzed according to CFR Title 40 specifications, and all applicable accuracy and calibration requirements were met. All filters were conditioned and weighed in accordance with the appropriate sections of the CFR for heavy-duty engines. Two sizes of filters were used to collect particulate samples. These filters included the following for each test:

- One set of 90-mm Pallflex (fluorocarbon-coated glass fiber) filters for determination of the regulated total particulate mass rate,
- One 20×20-inch Pallflex filter for dilute exhaust filtration of particulate and subsequent extraction for PAH and NPAH.

Analyses of unregulated emissions were conducted according to Coordinating Research Council (CRC), EPA, and SwRI analytical procedures. Applicable SwRI TIPs are listed in References 1 through 17. Table 4 presents the sampling requirements for each of the measured emissions, and Figure 4 shows a drawing of the engine, dilution tunnel, and sampling locations. Wet absorption techniques were employed to collect aldehydes and ketones. These wet absorption techniques are discussed in more detail below.

#### 3.1 Regulated Emissions

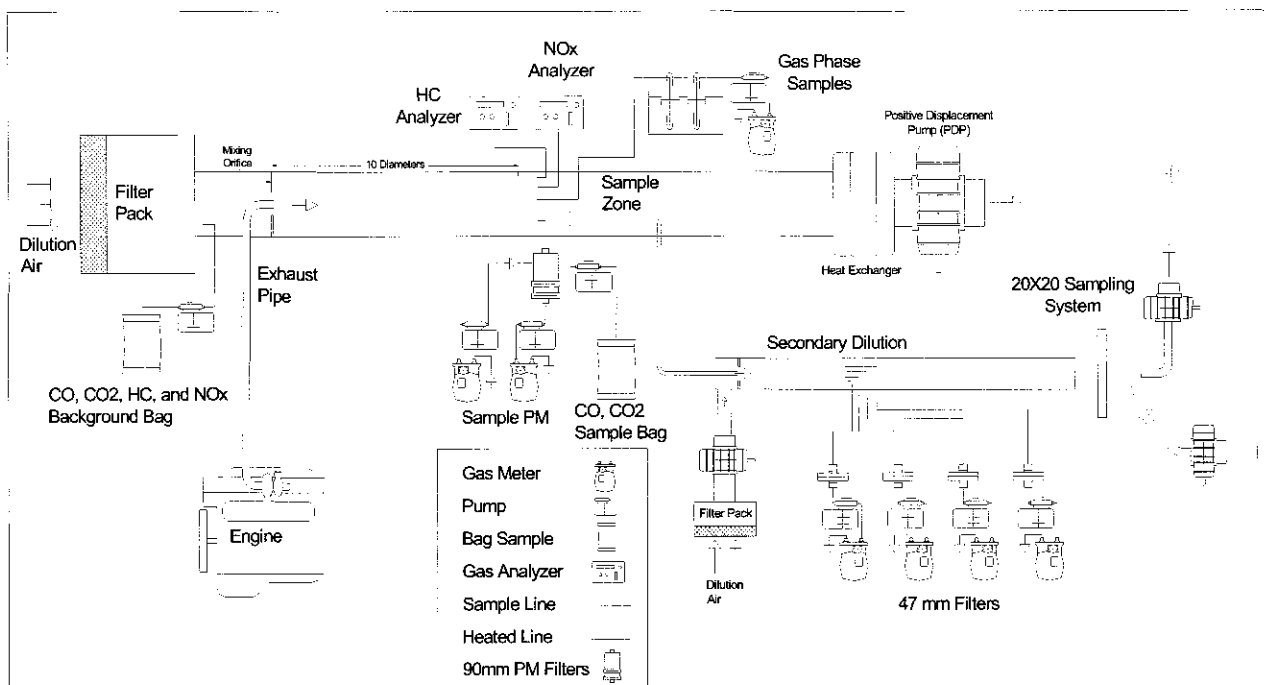
Regulated emissions were quantified in a manner consistent with EPA protocols for heavy-duty emissions testing as given in Title 40 CFR Part 86, Subpart N. Analysis of the regulated emissions was performed continuously throughout the entire test. The exhaust gas samples for CO and CO<sub>2</sub> were collected in Tedlar bags and analyzed using non-dispersive infrared (NDIR) instruments, and the THC and NO<sub>x</sub> were monitored continuously using a flame ionization detector and a chemiluminescent instrument, respectively.

**TABLE 4. SAMPLE COLLECTION**

Test Code	Test Day	Regulated THC, CO, NO <sub>x</sub> , Part.	Speciation C <sub>1</sub> – C <sub>12</sub>	PAH/NPAH		Aldehydes and Ketones
				Particulate	Volatile	
NPBASECAT-C1 <sup>b</sup>	1	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPBASECAT-H1		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPBASECAT-H2		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H3		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H4		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H5		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H6		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-C2	2	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPBASECAT-H7		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPBASECAT-H8		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H9		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H10		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H11		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H12		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-C3	3	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPBASECAT-H13		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPBASECAT-H14		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H15		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H16		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H17		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASECAT-H18		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-C1 <sup>c</sup>	4	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPBASE-H1		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPBASE-H2		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H3		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H4		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H5		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H6		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-C2	5	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPBASE-H7		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPBASE-H8		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H9		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H10		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H11		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H12		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-C3	6	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPBASE-H13		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPBASE-H14		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H15		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H16		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H17		Cont., Bag, 90mm Filter		20 X20 Filter		
NPBASE-H18		Cont., Bag, 90mm Filter		20 X20 Filter		

**TABLE 4 (CONT'D). SAMPLE COLLECTION**

Test Code	Test Day	Regulated THC, CO, NO <sub>x</sub> , Part.	Speciation C <sub>1</sub> – C <sub>12</sub>	PAH/NPAH		Aldehydes and Ketones
				Particulate	Volatile	
NPADDCAT-C1 <sup>b</sup>	1	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPADDCAT-H1		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPADDCAT-H2		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H3		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H4		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H5		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H6		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-C2	2	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPADDCAT-H7		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPADDCAT-H8		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H9		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H10		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H11		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H12		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-C3	3	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPADDCAT-H13		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPADDCAT-H14		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H15		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H16		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H17		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADDCAT-H18		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-C1 <sup>c</sup>	4	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPADD-H1		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPADD-H2		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H3		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H4		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H5		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H6		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-C2	5	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPADD-H7		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPADD-H8		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H9		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H10		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H11		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H12		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-C3	6	Cont., Bag, 90mm Filter	Bag	20 X20 Filter	PUF Trap	Bubbler
NPADD-H13		Cont., Bag, 90mm Filter	Bag	20 X20 Filter		Bubbler
NPADD-H14		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H15		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H16		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H17		Cont., Bag, 90mm Filter		20 X20 Filter		
NPADD-H18		Cont., Bag, 90mm Filter		20 X20 Filter		



**FIGURE 4. SAMPLE SYSTEM SCHEMATIC FOR EXHAUST EMISSION MEASUREMENTS**

### 3.2 Speciation of Volatile Hydrocarbon Compounds

Volatile hydrocarbon compounds were determined by hydrocarbon speciation. Analytical procedures for conducting the hydrocarbon speciation ( $C_1$  to  $C_{12}$  hydrocarbons, aldehydes, and ketones) were similar to the CRC Auto/Oil Phase II methods. The SwRI TIPs for this determination are listed in Reference Section. With these methods, exhaust emissions samples are analyzed for the presence of more than 200 different exhaust species. Four gas chromatography (GC) procedures and one High Performance Liquid Chromatography (HPLC) procedure were used to identify and quantify specific compounds. One GC is used for the measurement of methane, a second for  $C_2$ - $C_4$  species, and a third for  $C_5$ - $C_{12}$  species including three ethers (methyl tertiary butyl ether – MTBE, ethyl tertiary butyl ether – ETBE, and diisopropyl ether – DIPE). A fourth GC was used to measure 1-methylcyclopentane, benzene, toluene, and 2,3,3-trimethylpentane, which co-elute and cannot be accurately quantified by other methods. Analysis of all emission “sample” bags were begun within 30 minutes of sampling and before the “background” bags, so that reactive exhaust compounds could be analyzed as quickly as possible. Data were reported as background corrected. A brief description of these procedures is given in the following sections.

#### 3.2.1 Methane Speciation

Methane levels were determined for proportional exhaust gas samples collected in Tedlar bags and as described in SwRI TIP 07C-002. A GC equipped with a flame ionization detector (FID) was utilized for the analyses, and was used in accordance with SAE J1151 procedures. The GC system was equipped with a packed column to resolve methane from other hydrocarbons

in the sample. Samples were introduced into a 5-mL sample loop via a diaphragm pump. For analysis, the valve was switched to the inject position, and the helium carrier gas swept the sample from the loop toward the detector through a 61 cm  $\times$  0.3 cm Porapak N column in series with a 122 cm  $\times$  0.3 cm molecular sieve 13X column. As soon as the methane peak passed into the molecular sieve column, the helium flow was reversed through the Porapak N column to vent. For quantification, sample peak areas were compared to those of external calibration standards. Detection limits for the procedure were on the order of 0.05 mg/bhp-hr in dilute exhaust.

### 3.2.2 *C<sub>2</sub>-C<sub>4</sub> Species*

SwRI TIP 07C-013 describes the analytical procedure for determining the C<sub>2</sub>-C<sub>4</sub> hydrocarbons. With the aid of a DB-WAX pre-column and a 10-port switching valve, this procedure allowed the separation and determination of exhaust concentrations of C<sub>2</sub>-C<sub>4</sub> individual hydrocarbon species, including: ethane; ethylene; acetylene; propane; dimethylpropane; propyne; 1,3-butadiene; 2-methylpropane; 1-butyne; and cis-2-butene. Bag samples were analyzed with a GC system which utilized a Hewlett-Packard Model 5890 Series II GC with an FID, two pneumatically operated and electrically controlled valves, and two analytical columns. The first column separated the C<sub>2</sub>-C<sub>4</sub> hydrocarbons from the higher molecular weight hydrocarbons and the polar compounds. These higher molecular weight hydrocarbons (and water and alcohols) were retained on the pre-column while the C<sub>2</sub>-C<sub>4</sub> hydrocarbons were passed through to the analytical column. At the same time, the C<sub>2</sub>-C<sub>4</sub> hydrocarbons were separated on the analytical column, the pre-column was back-flushed with helium to prepare for the next analysis. The carrier gas for this analysis was helium. The column flow was set by fine-tuning the column head pressure to give butane a retention time of  $5.25 \pm 0.05$  minutes. The GC was calibrated daily using a CRC Auto/Oil 23-component calibration mixture. Analysis for the C<sub>2</sub>-C<sub>4</sub> hydrocarbons were typically begun within 30 minutes after sample collection is completed. Detection limits for the procedure were on the order of 0.05 mg/bhp-hr in dilute exhaust for all compounds.

### 3.2.3 *C<sub>5</sub>-C<sub>12</sub> Species*

SwRI TIP 07C-013 describes the analytical procedures for the C<sub>5</sub>-C<sub>12</sub> hydrocarbons. This procedure provides separation and exhaust concentrations for more than 100 C<sub>5</sub>-C<sub>12</sub> individual hydrocarbon compounds. Bag samples were analyzed using a gas chromatograph equipped with an FID. The GC system utilized a Hewlett-Packard Model 5890 Series II GC with an FID, a pneumatically operated and electrically controlled valve, and a DB-1 fused silica open tubular (FSOT) column. The carrier gas was helium. Gaseous samples were pumped from the bag through a sample loop and then introduced into a liquid nitrogen cooled column. The column oven was then programmed to a maximum temperature of 200°C. The analog signal from the FID was sent to a networked computer system via a buffered analog to digital converter. Column flow was set by fine-tuning the column head pressure to give propane a retention time of  $5.40 \pm 0.10$  minutes using a temperature program. The GC was calibrated daily using a CRC Auto/Oil 23-component calibration mixture. Detection limits for the procedure were on the order of 0.05 mg/bhp-hr in dilute exhaust for all compounds.

### 3.2.4 Benzene and Toluene

The analytical procedure for benzene and toluene is also described in SwRI TIP 07C-013. This procedure used a separate system configured similarly to the third GC method (with a DB-5 analytical column in place of a DB-1 FSOT column) to resolve individual concentrations of benzene and toluene according to the CRC Auto/Oil Phase II Protocols. Separation of benzene and toluene from co-eluting peaks was carried out by fine-tuning the column head pressure to give benzene a retention time of 22 to 23 minutes. The GC was calibrated daily using a CRC 7-component calibration mixture. Detection limits for the procedure were 0.05 mg/bhp-hr in dilute exhaust for all compounds.

### 3.2.5 Aldehydes and Ketones

An HPLC procedure was used for the analysis of aldehydes and ketones. SwRI TIP 07C-006 describes the procedure. Samples were collected by bubbling dilute exhaust at a nominal flowrate of 4 L/min through chilled glass impingers containing an acetonitrile solution of 2,4-DNPH and perchloric acid. Samples were transferred into volumetric flasks with ground glass joints and analyzed immediately or stored in ground glass stopped vials at 0°C for no more than one week prior to analysis. For analysis, a portion of the acetonitrile solution was injected into a liquid chromatograph equipped with an ultra-violet (UV) detector. External standards of the aldehyde and ketone DNPH derivatives were used to quantify the results. The aldehydes and ketones include: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, isobutyraldehyde/methylethylketone (not resolved from each other during normal operating conditions, and so split equally between the two compounds), benzaldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde/p-tolualdehyde (not resolved from each other during normal operating conditions, and so reported together), and hexanaldehyde. Detection limits for this procedure were on the order of 0.05 mg/bhp-hr aldehyde or ketone in dilute exhaust.

## 3.3 PAH and NPAH

In addition to the regulated and C<sub>1</sub> to C<sub>12</sub> hydrocarbon exhaust emissions, semi-volatile (volatile- and particulate-phase) PAH and NPAH compounds were also determined for each fuel. Seven PAH compounds were quantified: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene; and five NPAH compounds: 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene. A 400 in<sup>2</sup> fluorocarbon-coated glass fiber filter (20×20-inch Pallflex filter) was used to collect the particulate-phase PAH and NPAH, and a PUF/XAD/PUF sandwich adsorbent trap was used to collect the volatile-phase PAH and NPAH. The PUF/XAD/PUF traps contained a layered sampling media consisting of a 1.25 inch deep layer of polyurethane foam (PUF), a 0.5 inch deep layer of XAD-2 resin, and a second 1.25 inch deep layer of PUF. The XAD-2 resin was incorporated to improve the trapping efficiency for the lighter PAH and NPAH compounds.

Both XAD-2 and PUF sample media were cleaned prior to use. First, the XAD-2 was cleaned by siphoning four times with water using a Soxhlet. The residual water was then removed under vacuum. The XAD-2 was Soxhlet extracted three times: once with methanol for 24 hours, once with toluene for 48 hours, and finally with methylene chloride again for 48 hours.

The residual methylene chloride was removed by purging with heated nitrogen. For PUF cleaning, each foam disk was Soxhlet extracted three times: once for 24 hours with acetone, once for 48 hours with hexane/ether, and finally for 24 hours with acetone.

Volatile-phase PAH and NPAH samples presented a particular problem for heavy-duty sampling because conventional sampling techniques would not allow for sufficient sample to be gathered to meet EPA detection requirements. Commercially available sampling media and hardware were of insufficient size to allow for the collection of sample volumes needed to meet these detection limits. Sampling media size was also limited by the ability to extract and concentrate samples obtained. Therefore, an approach was devised involving both custom built sampling hardware and a modified sampling plan. The PUF/XAD/PUF traps were sized to allow a media diameter of 4 inches, rather than the conventional 2.5 inches. This larger diameter allowed a much higher flowrate to be used, while maintaining the face velocity within recommended levels for the smaller, conventional sampling media. This volume of dilute exhaust sample was sufficient for the analysis to meet a detection threshold of 1 ng/hp-hr.

Volatile- and particulate-phase PAH and NPAH samples were obtained using a separate secondary dilution tunnel, which was operated in parallel with the smaller secondary dilution tunnel used to obtain the 90-mm filter samples for particulate mass determinations. The PAH and NPAH tunnel was considerably larger than the 90-mm system in order to allow for the use of 20×20-inch Pallflex sampling media to collect particulate-phase PAH and NPAH compounds and to allow the use of a specially designed PUF/XAD/PUF trap to collect the volatile-phase PAH and NPAH compounds. Filter and PUF/XAD/PUF trap samples were generated during each cold-start and a hot-start test. Background PAH and NPAH sample sets were obtained by operating the sampling systems for about two hours with sampling media loaded, but without the engine operating.

Following testing, sample sets were delivered to the analytical laboratory for analysis. In cases where immediate extraction was not possible, samples were stored at 4°C. One half of each filter and the entire PUF/XAD/PUF sample material were extracted separately. Prior to extraction of the filters, each filter was spiked with a surrogate solution containing 100 ng each of six deuterated PAH:

- Benzo[a]anthracene-d12
- Chrysene-d12
- Benzo[b]fluoranthene-d12
- Benzo[k]fluoranthene-d12
- Benzo[a]pyrene
- Dibenzo[a,h]anthracene-d14

and four deuterated NPAH:

- 2-nitrofluorene-d9
- 1-nitropyrene-d9
- 6-nitrochrysene-d11
- 6-nitrobenzo[a]pyrene-d11.

This surrogate spike solution was used to verify sample recovery during the extraction process. The filters were then extracted by sonication three times each for 15 minutes (70/30 v/v toluene/ethanol the first two times and toluene the third time). For the PUF/XAD/PUF traps, each was spiked with the same amount of deuterated PAH and NPAH as used for the filters. The trap samples were then extracted for at least 8 hours with methylene chloride. After extraction, the methylene chloride extract was reduced to 20 mL with a rotary evaporator with a water bath held at 35°C. The concentrated extract was then split into three portions: two 8 mL and one 4 mL. Both 8 mL extracts were solvent exchanged to hexane, cleaned with silica gel, and blown down to 100 µL. One 100 µL extract sample was utilized for PAH analysis, while the second was utilized for NPAH analysis. The 4 mL extract was saved as a reserve. The filter extract was treated similarly as the trap extract except that this extract was split into two even parts with one for PAH analysis and the other for NPAH analysis. Each unextracted filter half was saved as a reserve.

Samples for both the volatile- and the particulate-phase PAH and NPAH were analyzed by GC/MS (gas chromatograph/mass spectroscopy) using an Agilent 5973N MSD 30 m by 0.25 mm i.d. DB-5 column with a 0.25 mm film thickness. For each analysis, an 1 µL aliquot of the sample extract was injected into the instrument. A calibration curve consisting of at least five points was obtained prior to sample analysis to ensure linearity, and a mid-point continuing calibration was performed each day after the initial five point calibration. Analysis of NPAH compounds was performed using the negative ion/chemical ionization (NI/CI) mode and analysis for PAH compounds was performed using the positive ion/electron ionization (PI/EI) mode. Two or three characteristic ions for each PAH and NPAH were monitored. Separate GC/MS analyses were necessary to acquire both the PAH and NPAH data. Each target compound met the criterion of a 30 percent relative response factor (RRF) and 30 percent deviation in relation to the mean RRF obtained in the initial and continuing calibration.



## 4.0 QUALITY CONTROL AND QUALITY ASSURANCE

In order to demonstrate SwRI's constant goal to provide quality emissions data in our project efforts, the Engine, Emissions, and Vehicle Research Division (EEVRD) maintains certification to ISO 9001:2000 and accreditation to ISO/IEC 17025:2005 standards. Standard operating procedures and routine instrument calibration and calibration records are included in these standards. Based on the successful completion of third party audits, the EEVRD is able to maintain registration under ISO 9001:2000, "Quality Management System," and accreditation by ISO/IEC 17025:2005, General Requirements for the Competence of Testing and Calibration Laboratories." The SwRI Office of Automotive Engineering (OAE) Quality Policy Statement:

### SwRI OAE Quality Policy Statement

*"The Office of Automotive Engineering provides unequalled capabilities for the research, development, evaluation, and qualification of transportation systems, vehicles, engines, fuels, lubricants, and emissions-related products. Quality excellence is the foundation for the management of our business and the keystone to customer satisfaction. It is our objective to ensure that our final products are internationally recognized with unquestioned quality and are delivered to our clients in a professional, cost effective, and timely manner."*

*"We are committed to comply with ISO 17025, ISO 9001:2000, and all customer-required standards of excellence. Continual improvement of this policy occurs through regular review of the quality system's suitability to meet customer, employee, and supplier needs."*

Throughout this project, SwRI implemented our QA/QC plan in a manner consistent with the program objectives, including spot-checking of records, accuracy/precision charts, notebooks, calibration tags, and other quality control elements including chain of custody of samples. Listed below are a few of the key process that ensure the quality standards are implemented.

**Senior Scientist/Technician Review** - A system for formal data review is in place in the SwRI Emissions Research and Development Department (ER&DD). All technicians review their work prior to submitting it to the data computations laboratory for calculation of final concentrations. The Project Leader performs the final review before test results are accepted.

**Interlaboratory Comparisons/Round Robins** - SwRI has participated in numerous Round Robin exercises to correlate the results of our laboratory with other accepted facilities. Those Round Robin studies which are directly related to this project include: CRC Round Robin Analysis of Alcohol and Carbonyl Synthetic Exhaust Samples (results published in SAE Paper No. 941944); and CRC Round Robin Hydrocarbon Speciation Analysis of Synthetic Exhaust Gas (results not published).

**Project Records** - Documents directly associated with a technical project, such as: correspondence, proposals, contracts, work orders, interim and final reports, and follow-up contacts are maintained. These records are handled in accordance with Standard Operating Procedure (SOP), document SOP-4.16 "Quality Records" (Reference 17).

**Calibration Records** - Data sheets, chart recordings, computer printouts, logbooks, calibration and maintenance logs, and spreadsheets associated with the calibration of measurement equipment are maintained. Calibration results from external suppliers are also included.

**Engine and Vehicle Testing Records** - Data sheets, chart recordings, logbooks, start/stop logs, and computer printouts associated with evaluation and testing of engines and vehicles are retained.

**Chemistry Calibration and Analysis Records** - Data sheets, logbooks, and spreadsheets associated with calibration and analyses performed in the chemistry areas are retained.

**Data Reduction and Test Result Records** - Computed results, tables, and spreadsheets generated using information obtained from emissions testing and chemical analysis are maintained. Records developed in the areas specified in SOP 4.16 are retained for a period of ten years.

**Training and Competency Evaluation:** Personnel are trained to applicable SOP, TIP, and Design and Analysis Procedures and Safety Requirements. Staff members that perform an individual test are certified before performing these tests without supervision. Management encourages personnel to avail themselves to attend appropriate seminars, conferences, and continuing/higher education opportunities to continually enhance their skill set.

## 5.0 TEST RESULTS

Emissions testing was performed using a 2007 6.4 L Navistar A350 heavy-duty diesel engine. This engine was operated for 125 hours with both fuels: a baseline fuel and a neat NExBTL™ renewable diesel. Tests were performed after each 125 hours period of engine operation. Four cold- and 24 hot-start tests were conducted to characterize emissions at each test point. Two cold- and 12 hot-start test sequences were conducted with the engine exhaust aftertreatment in place, and two cold- and 12 hot-start test sequences were performed with the aftertreatment removed.

### 5.1 Regulated Emissions

After 125 hours of engine operation with the baseline fuel, the average composite emissions were significantly lower than the corresponding 2007 emission standard. The 2007 emission standards limit the sum of the NMHC and NO<sub>x</sub> (NMHC + NO<sub>x</sub>) to 2.4 g/bhp-hr or to 2.5 g/bhp-hr if the NMHC do not exceed 0.5 g/bhp-hr. In this case, the average composite emissions were 1.0 g/bhp-hr for NO<sub>x</sub> both with and without aftertreatment, 0.18 g/bhp-hr for NMHC with no aftertreatment, and 0.02 g/bhp-hr for NMHC with aftertreatment. For particulate, the average composite emissions were less than 0.01 g/bhp-hr with aftertreatment and 0.31 g/bhp-hr without aftertreatment. The particulate measurement with no aftertreatment exceeded the 2007 particulate standard of 0.10 g/bhp-hr, but the engine could not be expected to meet the standard without aftertreatment. The CO emissions averaged 0.5 g/bhp-hr with aftertreatment and 3.5 g/bhp-hr without aftertreatment which did not exceed the 15.5 g./bhp-hr 2007 standard with the baseline fuel.

After 125 hours of engine operation with neat NExBTL™ renewable diesel, the NO<sub>x</sub> and particulate emissions were slightly lower than with the initial tests with the baseline fuel. The NMHC + NO<sub>x</sub> and particulate emissions were 0.8 and 0.01 g/bhp-hr, respectively, with aftertreatment and 0.9 and 0.29 g/bhp-hr, respectively, without aftertreatment. The percent reduction in NO<sub>x</sub> was about 17 percent with aftertreatment and about 13 percent without aftertreatment when compared to the baseline fuel. No relative change was noted for the particulate with aftertreatment, and a 6 percent reduction was observed with no aftertreatment when compared to the baseline fuel. A 0.05 g/bhp-hr increase in the CO was measured with aftertreatment, and a 1.0 g/bhp-hr decrease was observed without aftertreatment when compared to the baseline fuel. No relative change was noted for the NMHC with aftertreatment, and a 58 percent reduction was observed for the NMHC with no aftertreatment when compared to the baseline fuel. Table 5 summarizes the regulated emissions at each test condition, and Figures 5 through 7 illustrate the regulated emissions both with and without aftertreatment for each fuel. Appendix A contains the individual and composite emission test results.

### 5.2 Speciation of Volatile Hydrocarbon Compounds

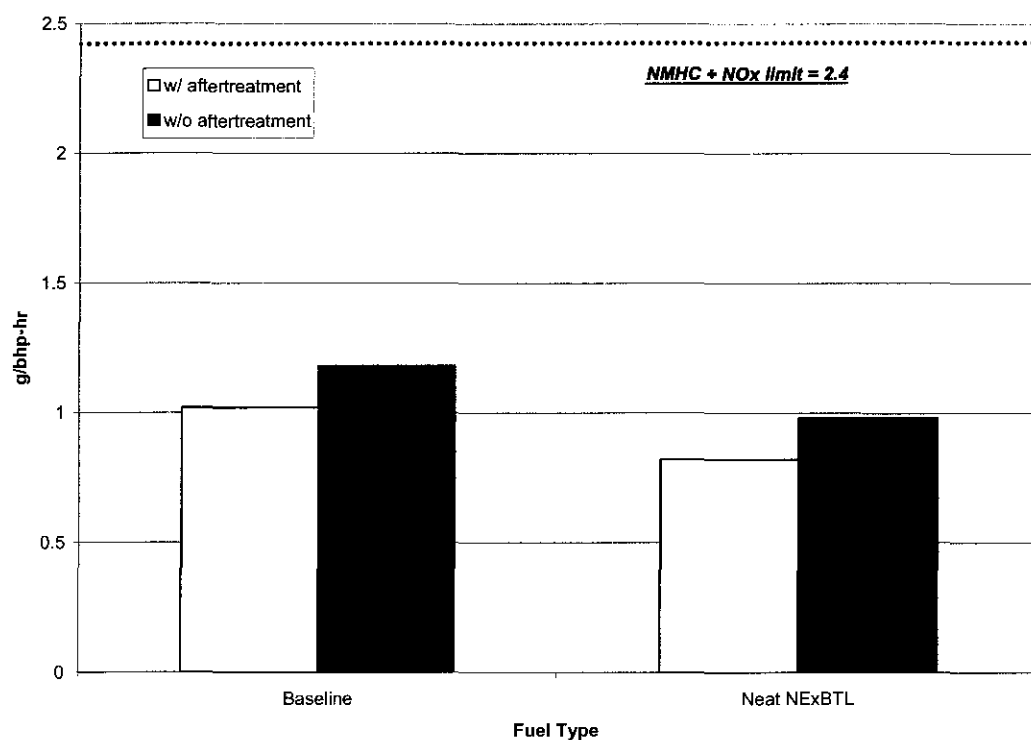
Speciation results for volatile hydrocarbon compounds with carbon numbers from C<sub>1</sub> to C<sub>12</sub> plus aldehydes, ketones, and three ethers (methyl tertiary butyl ether - MTBE, ethyl tertiary butyl ether - ETBE, and di-isopropyl ether - DIPE) are included in this section. Speciation was performed on samples collected during each cold- and hot-start test sequence both with and without the aftertreatment. More than 200 compounds were checked for their presence in the

**TABLE 5. SUMMARY OF REGULATED EMISSIONS**

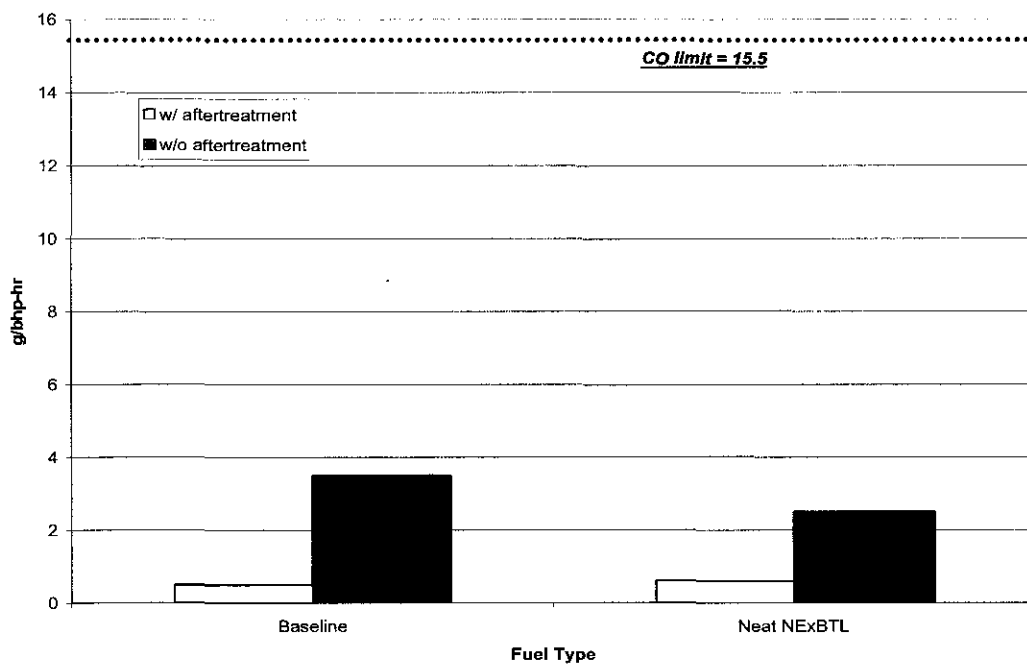
Test	Emissions Results, g/bhp-hr			
	NMHC	CO	NO <sub>x</sub>	Particulate
<b>Baseline Fuel With Aftertreatment (Initial Test)</b>				
NPBASECAT C1	0.07	0.8	1.3	0.01
NPBASECAT H1	0.00	0.5	1.0	0.01
Composite C1-H1	0.01	0.6	1.0	0.01
NPBASECAT C2	0.04	0.5	1.2	0.01
NPBASECAT H7	0.01	0.4	1.0	0.01
Composite C2-H7	0.02	0.4	1.0	0.01
NPBASECAT C3	0.05	0.6	1.1	0.01
NPBASECAT H13	0.01	0.5	0.9	0.00
Composite C3-H13	0.02	0.5	0.9	0.00
Average of Composites	0.02	0.5	1.0	0.01
<b>Baseline Fuel Without Aftertreatment (Initial Test)</b>				
NPBASE C1	0.22	3.6	1.2	0.33
NPBASE H1	0.17	3.6	1.0	0.32
Composite C1-H1	0.18	3.6	1.0	0.32
NPBASE C2	0.21	3.4	1.2	0.30
NPBASE H7	0.17	3.5	1.0	0.30
Composite C2-H7	0.18	3.4	1.0	0.30
NPBASE C3	0.21	3.3	1.2	0.30
NPBASE H13	0.17	3.4	1.0	0.31
Composite C3-H13	0.18	3.4	1.0	0.31
Average of Composites	0.18	3.5	1.0	0.31
<b>Neat NExBTL™ With Aftertreatment After 125 Hours</b>				
NPADDCAT C1	0.03	0.7	0.9	0.01
NPADDCAT H1	0.02	0.6	0.8	0.01
Composite C1-H1	0.02	0.6	0.8	0.01
NPADDCAT C2	0.02	0.6	1.0	0.01
NPADDCAT H7	0.02	0.5	0.8	0.01
Composite C2-H7	0.02	0.5	0.8	0.01
NPADDCAT C3	0.02	0.6	0.9	0.01
NPADDCAT H13	0.02	0.5	0.8	0.01
Composite C3-H13	0.02	0.5	0.8	0.01
Average of Composites	0.02	0.6	0.8	0.01

**TABLE 5 (CONT'D). SUMMARY OF REGULATED EMISSIONS**

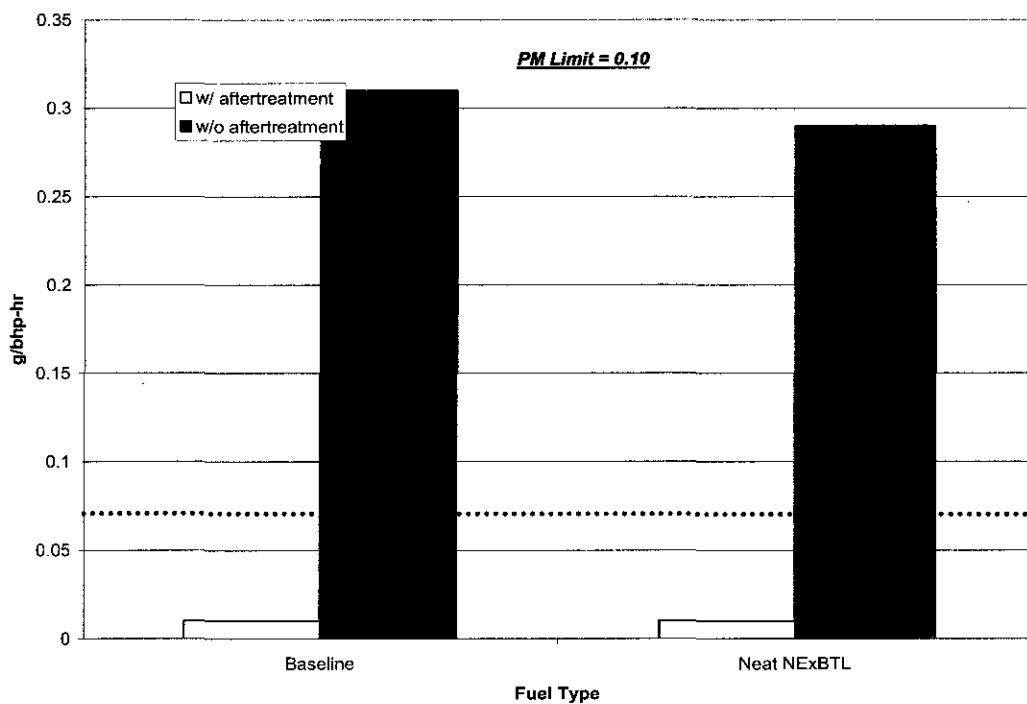
Test	Emissions Results, g/bhp-hr			
	NMHC	CO	NO <sub>x</sub>	Particulate
<b>Neat NExBTL™ Without Aftertreatment After 125 Hours</b>				
NPADD C1	0.08	2.6	1.0	0.34
NPADD H1	0.09	2.6	0.8	0.31
Composite C1-H1	0.09	2.6	0.9	0.31
NPADD C2	0.08	2.5	1.0	0.27
NPADD H7	0.08	2.5	0.8	0.28
Composite C2-H7	0.08	2.5	0.9	0.28
NPADD C3	0.06	2.4	1.0	0.30
NPADD H13	0.05	2.4	0.9	0.29
Composite C3-H13	0.05	2.4	0.9	0.29
Average of Composites	0.08	2.5	0.9	0.29



**FIGURE 5. COMPARISON OF NO<sub>x</sub> EMISSIONS BOTH WITH AND WITHOUT AFTERTREATMENT**



**FIGURE 6. COMPARISON OF CO EMISSIONS BOTH WITH AND WITHOUT AFTERTREATMENT**



**FIGURE 7. COMPARISON OF PARTICULATE EMISSIONS BOTH WITH AND WITHOUT AFTERTREATMENT**

dilute exhaust. Data for the individual compounds, corrected for background dilution air contributions, are included in Appendix B.

In general, all compounds found in the exhaust with neat NExBTL™ renewable diesel were also found in the exhaust with the baseline fuel. No additional compounds were found in the exhaust from engine operation with NExBTL™ fuel as compared to the baseline fuel at or above the detection limits for the analytical procedures. While no additional compounds could be identified with these fuels, some differences did occur in the individual concentrations, and a large number of compounds were detected in the tests with the baseline fuel without aftertreatment that were not detected with the neat NExBTL™ fuel without aftertreatment. These compounds included:

- |                                      |                                |
|--------------------------------------|--------------------------------|
| • propadiene                         | • nonane                       |
| • 1-butene                           | • 2,4-dimethyloctane           |
| • 2,2-dimethylpropane                | • n-propylbenzene              |
| • cis-2-butene                       | • 1-methyl-3-ethylbenzene      |
| • 2-methylbutane                     | • 1,3,5-trimethylbenzene       |
| • 1-pentene                          | • 1-methyl-2-ethylbenzene      |
| • 2-methyl-1-butene                  | • 1,2,4-trimethylbenzene       |
| • unidentified C <sub>5</sub> olefin | • decane                       |
| • trans-2-pentene                    | • isobutylbenzene              |
| • 2-methyl-2-butene                  | • 1-methyl-3-isopropylbenzene  |
| • 2,2-dimethylbutane                 | • 1-methyl-2-isopropylbenzene  |
| • cyclopentane                       | • 1,4-diethylbenzene           |
| • 3-methyl-trans-2-pentene           | • 1-methyl-3-n-propylbenzene   |
| • 2,4-dimethylpentane                | • 1,2-diethylbenzene           |
| • 3,4-dimethyl-1-pentene             | • 1,4-dimethyl-2-ethylbenzene  |
| • unidentified C <sub>7</sub>        | • 1,2-dimethyl-4-ethylbenzene  |
| • methylcyclohexane                  | • undecane                     |
| • 2,4-dimethylhexane                 | • 1,2,4,5-tetramethylbenzene   |
| • 2,3,4-trimethylpentane             | • tert-1-butyl-2-methylbenzene |
| • unidentified C <sub>8</sub>        | • 1,2,3,4-tetramethylbenzene   |
| • 2,4-dimethyleheptane               | • n-pentylbenzene              |
| • 2,6-dimethylheptane                | • benzaldehyde                 |
| • ethylbenzene                       | • dimethylbenzaldehyde         |
| • 1-nonene                           |                                |

Some compounds that were found in the baseline exhaust with aftertreatment were not found with the neat NExBTL™ with aftertreatment. These compounds included:

- |                          |                                    |
|--------------------------|------------------------------------|
| • 2-methylpropene        | • 2,2-dimethylpentane              |
| • 1,3-butadiene          | • methylcyclopentane               |
| • 2-methyl-1,3-butadiene | • 2,3-dimethylpentane              |
| • cyclopentadiene        | • cis-1,3-dimethylcyclopentane     |
| • cyclopentene           | • cis-1-methyl-3-ethylcyclopentane |
| • 4-methyl-1-pentene     | • octane                           |
| • 2-methyl-1-pentene     | • dodecane                         |
| • 1-hexene               | • o-tolualdehyde                   |

In any case, no additional compounds, which could be attributed to the presence of the additive, were found in the exhaust at the detection limits for the analytical procedures.

Some compounds were found in either one or more of the cold- or one or more of the hot-starts during the triplicate test sequence with each fuel, with or without the aftertreatment. Values were reported when these compounds were detected at more than two times the detection limit (0.05 mg/bhp-hr). In other cases, compounds were detected at less than two times the detection limit. In this case, the compounds are labeled as "trace" in the appendix tables. Where compounds are not detected or were less than the detection limit, ND was used to indicate that no quantitative value could be assigned to the compound for that test. Average values were also reported for each set of cold- or hot-start test for each test condition. For these averages, values reported as trace or ND were set to zero for calculation purposes.

### 5.3 PAH and NPAH

Volatile- and particulate-phase PAH and NPAH compounds were determined for each test condition. Individual compounds included: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene. The analytical procedure used to measure these compounds was able to detect less 1 ng/bhp-hr. Values have been reported in terms of ng/bhp-hr for each compound. Table 6 presents the volatile-phase results, and Table 7 presents the particulate-phase results. Table 8 summarizes the combined volatile- and particulate-phase results.

In general, concentrations of PAH and NPAH in the volatile-phase were lower than the concentrations of the PAH and NPAH in the particulate-phase, and the concentrations of PAH and NPAH were lower with aftertreatment than without it. Chrysene was the only compound detected in measurable amounts with aftertreatment in the volatile-phase. Without aftertreatment, 1-nitropyrene was detected at the highest concentration for the NPAHs, and the PAHs were generally higher in concentration than the NPAHs. A general trend was also noted for both fuels. The concentrations for most PAH and NPAH were greatest with the baseline fuel and least with the neat NExBTL™ renewable diesel. This trend was also observed when the PAH and NPAH were summed.



**TABLE 6. VOLATILE-PHASE SEMI-VOLATILE PAH AND NPAH RESULTS**

Compounds <sup>a</sup>	Base Fuel, ng/bhp-hr				Neat NExBTL™, ng/bhp-hr			
	1	2	3	Average	1	2	3	Average
<b>With Aftertreatment</b>								
2-Nitrofluorene	Trace <sup>b</sup>	ND <sup>c</sup>	0.5	Trace	Trace	Trace	Trace	Trace
1-Nitropyrene	ND	Trace	ND	Trace	Trace	Trace	Trace	Trace
7-Nitrobenz(a)anthracene	ND	0.9	Trace	Trace	ND	ND	Trace	Trace
6-Nitrochrysene	ND	ND	ND	ND	ND	ND	ND	ND
6-Nitrobenz(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	ND	ND	Trace	Trace	Trace	0.4	Trace	Trace
Chrysene	4.7	1.6	0.4	2.2	1.6	1.3	3.6	2.2
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	Trace	Trace	Trace
Benzo(k)fluoranthene	ND	ND	ND	ND	Trace	Trace	Trace	Trace
Benzo(a)pyrene	ND	ND	ND	ND	Trace	Trace	Trace	Trace
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	ND	ND	Trace	Trace
Dibenz(a,h)anthracene	Trace	0.3	Trace	Trace	0.6	Trace	Trace	Trace
<b>Without Aftertreatment</b>								
2-Nitrofluorene	0.3	0.5	Trace	0.3	Trace	ND	5.0	1.7
1-Nitropyrene	Trace	0.4	0.3	Trace	Trace	Trace	Trace	Trace
7-Nitrobenz(a)anthracene	4.6	7.3	7.0	6.3	ND	0.3	ND	Trace
6-Nitrochrysene	ND	ND	ND	ND	ND	ND	1.6	0.5
6-Nitrobenz(a)pyrene	ND	ND	ND	ND	1.6	2.5	2.2	2.1
Benzo(a)anthracene	0.4	0.4	0.7	0.5	Trace	0.5	0.3	0.3
Chrysene	Trace	ND	ND	Trace	ND	0.5	0.4	0.3
Benzo(b)fluoranthene	Trace	Trace	0.5	Trace	Trace	1.1	1.0	0.7
Benzo(k)fluoranthene	ND	ND	Trace	Trace	Trace	0.4	0.3	Trace
Benzo(a)pyrene	Trace	Trace	0.4	Trace	0.5	0.9	0.7	0.7
Indeno[1,2,3-cd]pyrene	ND	ND	Trace	Trace	ND	ND	ND	ND
Dibenz(a,h)anthracene	Trace	Trace	0.4	Trace	0.6	0.8	0.9	0.8
<sup>a</sup> Detection limit in ng/bhp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 0.2 ng/bhp-hr. <sup>b</sup> Trace - Value not quantifiable at detection limit; concentration less than twice the detection limit <sup>c</sup> ND - None detected at the detection limit.								

**TABLE 7. PARTICULATE-PHASE SEMI-VOLATILE PAH AND NPAH RESULTS**

Compounds <sup>a</sup>	C1-H6, ng/bhp-hr			C2-H12, ng/bhp-hr			C3-H18, ng/bhp-hr			Average Composite, ng/bhp-hr
	Cold	Hot	Composite	Cold	Hot	Composite	Cold	Hot	Composite	
Baseline Fuel With Aftertreatment										
2-Nitrofluorene	ND <sup>b</sup>	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Nitropyrene	5.7	ND	Trace <sup>c</sup>	ND	ND	ND	ND	ND	ND	Trace
7-Nitrobenz(a)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6-Nitrochrysene	4.4	ND	Trace	ND	ND	ND	ND	ND	ND	Trace
6-Nitrobenz(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	4.5	ND	Trace	3.2	ND	Trace	4.3	ND	Trace	Trace
Chrysene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(b)fluoranthene	3.1	ND	Trace	ND	ND	ND	4.3	ND	Trace	Trace
Benzo(k)fluoranthene	Trace	ND	Trace	Trace	ND	Trace	2.3	ND	Trace	Trace
Benzo(a)pyrene	6.8	ND	Trace	1.5	Trace	Trace	6.2	2.0	2.6	1.3
Indeno[1,2,3-cd]pyrene	2.2	ND	Trace	Trace	ND	Trace	3.7	ND	Trace	Trace
Dibenz(a,h)anthracene	Trace	ND	Trace	Trace	ND	Trace	1.2	ND	Trace	Trace
Baseline Fuel Without Aftertreatment										
2-Nitrofluorene	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
1-Nitropyrene	484	478	479	423	463	457	302	328	325	420
7-Nitrobenz(a)anthracene	ND	ND	ND	ND	ND	ND	36	ND	5.2	1.7
6-Nitrochrysene <sup>a</sup>	18	15	15	ND	13	11	11	13	13	13
6-Nitrobenz(a)pyrene	ND	184	158	ND	ND	ND	ND	ND	ND	53
Benzo(a)anthracene	1350	1440	1430	1460	1310	1330	1090	1410	1360	1370
Chrysene	2090	2080	2080	2270	1990	2030	1640	2080	2020	2040
Benzo(b)fluoranthene	1990	1880	1890	2050	1740	1780	1350	1840	1770	1810
Benzo(k)fluoranthene	613	585	589	616	548	558	427	584	562	570
Benzo(a)pyrene	2000	1820	1840	1950	1500	1570	1230	1530	1480	1630
Indeno[1,2,3-cd]pyrene	2710	1230	1440	1580	1330	1360	1200	1170	1170	1320
Dibenz(a,h)anthracene	177	122	130	157	120	125	92	114	111	122
<sup>a</sup> Detection limit in ng/bhp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 1 ng/bhp-hr.										
<sup>b</sup> ND - None detected at the detection limit										
<sup>c</sup> Trace - Value not quantifiable at detection limit; concentration less than twice the detection limit										

**TABLE 7 (CONT'D). PARTICULATE-PHASE SEMI-VOLATILE PAH AND NPAH RESULTS**

Compound <sup>a</sup>	C1-H6, ng/bhp-hr			C2-H12, ng/bhp-hr			C3-H18, ng/bhp-hr			Average Composite, ng/bhp-hr
	Cold	Hot	Composite	Cold	Hot	Composite	Cold	Hot	Composite	
Neat NExBTL™ With After treatment										
2-Nitrofluorene	Trace <sup>c</sup>	Trace	Trace	2.3	ND <sup>b</sup>	Trace	Trace	Trace	Trace	Trace
1-Nitropyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7-Nitrobenz(a)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6-Nitrochrysene	Trace	Trace	Trace	ND	Trace	Trace	ND	0.4	0.3	Trace
6-Nitrobenz(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Neat NExBTL™ Without After treatment										
2-Nitrofluorene	2.6	Trace	1.2	0.3	3.9	3.4	1.5	ND	Trace	1.1
1-Nitropyrene	325	462	442	333	355	352	329	259	269	354
7-Nitrobenz(a)anthracene	3.9	2.9	3.1	1.3	1.2	1.2	2.4	Trace	1.1	1.8
6-Nitrochrysene <sup>a</sup>	ND	ND	ND	ND	8.6	7.4	ND	ND	ND	2.5
6-Nitrobenz(a)pyrene	17	12	13	21	24	23	16	17	17	18
Benzo(a)anthracene	1180	1250	1240	1070	1100	1100	1300	1110	1140	1160
Chrysene	1410	1500	1480	1320	1290	1300	1600	1260	1310	1360
Benzo(b)fluoranthene	1780	1920	1900	1660	1610	1620	2100	1520	1600	1710
Benzo(k)fluoranthene	450	480	476	440	399	405	548	380	404	428
Benzo(a)pyrene	2100	2440	2440	2120	2140	2140	2750	177	544	1690
Indeno[1,2,3-cd]pyrene	1270	1760	1690	1550	1440	1460	2090	1080	1230	1460
Dibenz(a,h)anthracene	72	92	89	67	81	79	90	72	74	81
<sup>a</sup> Detection limit in ng/bhp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 1 ng/bhp-hr.										
<sup>b</sup> ND - None detected at the detection limit.										
<sup>c</sup> Trace - Value not quantifiable at detection limit; concentration less than twice the detection limit										

**TABLE 8. COMBINED VOLATILE- AND PARTICULATE-PHASE PAH AND NPAH RESULTS**

Compound <sup>a</sup>	Baseline Fuel, ng/bhp-hr			Neat NExBTL™, ng/bhp-hr		
	Volatile	Particulate	Total	Volatile	Particulate	Total
<b>With Aftertreatment</b>						
2-Nitrofluorene	Trace <sup>b</sup>	ND <sup>c</sup>	Trace	Trace	Trace	Trace
1-Nitropyrene	Trace	Trace	Trace	Trace	ND	Trace
7-Nitrobenz(a)anthracene	Trace	ND	Trace	Trace	ND	Trace
6-Nitrochrysene	ND	Trace	Trace	ND	Trace	Trace
6-Nitrobenz(a)pyrene	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	Trace	Trace	Trace	Trace	ND	Trace
Chrysene	2.2	ND	2.2	2.2	ND	2.2
Benzo(b)fluoranthene	ND	Trace	Trace	Trace	ND	Trace
Benzo(k)fluoranthene	ND	Trace	Trace	Trace	ND	Trace
Benzo(a)pyrene	ND	1.3	1.3	Trace	ND	Trace
Indeno[1,2,3-cd]pyrene	ND	Trace	Trace	Trace	ND	Trace
Dibenz(a,h)anthracene	Trace	Trace	Trace	Trace	ND	Trace
<b>Without Aftertreatment</b>						
2-Nitrofluorene	0.3	Trace	Trace	1.7	1.1	2.8
1-Nitropyrene	Trace	420	420	Trace	354	354
7-Nitrobenz(a)anthracene	6.3	1.7	8.0	Trace	1.8	1.8
6-Nitrochrysene	ND	13	13	0.5	2.5	3.0
6-Nitrobenz(a)pyrene	ND	53	53	2.1	18	20
Benzo(a)anthracene	0.5	1370	1370	0.3	1160	1160
Chrysene	Trace	2040	2040	0.3	1360	1360
Benzo(b)fluoranthene	Trace	1810	1810	0.7	1710	1710
Benzo(k)fluoranthene	Trace	570	570	Trace	428	428
Benzo(a)pyrene	Trace	1630	1630	0.7	1690	1690
Indeno[1,2,3-cd]pyrene	Trace	1320	1320	ND	1460	1460
Dibenz(a,h)anthracene	Trace	122	122	0.8	81	82
<sup>a</sup> Detection limit in ng/bhp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 1 ng/bhp-hr. <sup>b</sup> Trace - Value not quantifiable at detection limit; concentration less than twice the detection limit <sup>c</sup> ND - None detected at the detection limit.						

## 6.0. SUMMARY

Testing was performed on a heavy-duty engine to provide Neste Oil Corporation with data in support of the EPA requirements for registration of a designated F/FA as stipulated by section 211 (b) and 211 (e) of the CAA. A 2007 6.4 L Navistar A350 engine was tested according to procedures established in 40 CFR 79.57 and 40 CFR 86 Subpart D. Emissions characterization was performed on the engine after 125 hours of operation with the baseline fuel and after 125 hours of operation with neat NExBTL.

When the composite emissions for the neat NExBTL™ renewable diesel with aftertreatment were compared to the corresponding composite emissions from the baseline fuel, the NExBTL™ renewable diesel was found to produce regulated emission levels which were 0.05 g/bhp-hr higher for CO, 17 percent lower for NO<sub>x</sub>, and no relative change for NMHC and particulate. Similar trends were also observed when making comparisons without aftertreatment. In this case, the NO<sub>x</sub> emissions decreased by about 13 percent, the CO decreased by about 29 percent, the particulate emissions decreased by about 6 percent, and the NMHC decreased by 58 percent.

In general, the regulated emissions were higher with the aftertreatment disabled. The emissions were able to meet the 2007 emission standards for both fuels when the aftertreatment was in place; but without aftertreatment, the particulate emissions were not able to meet the standards for both fuels. This higher level of particulate emissions without aftertreatment was not unexpected because the aftertreatment was necessary for the engine to meet these standards.

Speciation of the C<sub>1</sub> to C<sub>12</sub> hydrocarbons, aldehydes, and ketones was performed during each cold- and hot-segment of the EPA transient cycle. In general,

- All compounds measured in the exhaust with neat NExBTL™ renewable diesel were also present in the exhaust with the baseline fuel
- No additional compounds, which could be attributed to the use of NExBTL™, were found in the exhaust at the detection limits for the analytical procedures.
- A large number of compounds were found only in the baseline fuel and were not found with neat NExBTL™.

While selected individual C<sub>1</sub> to C<sub>12</sub> hydrocarbons were determined to be below the detection limit, one cannot necessarily conclude that these compounds were present or not present; however if present, the compounds were below the limits of detection.

Volatile- and particulate-phase PAH and NPAH compounds were determined for each test condition. Individual compounds included: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene. In general, exhaust PAH and NPAH concentrations were higher in the particulate-phase than in the volatile-phase. Higher concentrations of PAH and NPAH were detected when the aftertreatment was removed. The total PAH and NPAH were higher with the baseline fuel and lowest with neat NExBTL™ renewable diesel.

## 7.0 REFERENCES

1. DER SwRI TIP 06-001, "Traceability to Standards."
2. DER SwRI TIP 06-002, "NO<sub>x</sub> Converter Efficiency Determination."
3. DER SwRI TIP 06-003, "Linearity Verification of Gas Dividers."
4. DER SwRI TIP 06-010, "Barometric Pressure Verification."
5. DER SwRI TIP 06-011, "Propane Recovery Check."
6. DER SwRI TIP 06-013, "Temperature Calibration and Verification."
7. DER SwRI TIP 06-016, "Wet CO<sub>2</sub> Interference Check for CO Analyzers."
8. DER SwRI TIP 06-020, "Pressure Calibration and Verification."
9. DER SwRI TIP 06-022, "CVS Blower Calibration."
10. DER SwRI TIP 06-023, "Calibration of Analyzers Using Digital Readout."
11. DER SwRI TIP 07-023, "Operation of Bag Cart."
12. DER SwRI TIP 07C-002, "Methane Quantitative Analysis."
13. DER SwRI TIP 07C-006, "Analysis of Aldehydes and Ketones in Exhaust by Liquid Chromatography."
14. DER SwRI TIP 07C-010, "Impinger Sampling of Exhaust Emissions."
15. DER SwRI TIP 07C-011, "Preparation of Impingers Used in Collection of Unregulated Emissions."
16. DER SwRI TIP 07C-013, "Hydrocarbon Speciation."
17. DER SwRI SOP-4.16, "Quality Records."